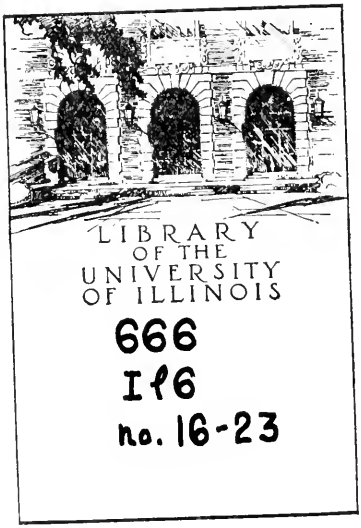

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THE INFLUENCE OF CHLORIDES OF CALCIUM AND IRON WHEN PRECIPITATED IN A PORCELAIN BODY

SOME COBALT-URANIUM COLORS

BY

B. S. RADCLIFFE

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THE INFLUENCES OF CALCIUM AND IRON CHLORIDES PRECIPITATED IN A PORCELAIN BODY

BY B. S. RADCLIFFE

The production of vitrified red floor tile has given manufacturers considerable trouble. Practically, the only solution of the problem has been to secure a good red burning clay, and burn to a degree of vitrification such that the red color is not destroyed. In most instances, it has been found impossible to make red bodies that have less than four or five percent absorption, and in many cases the absorption is considerably greater than this.

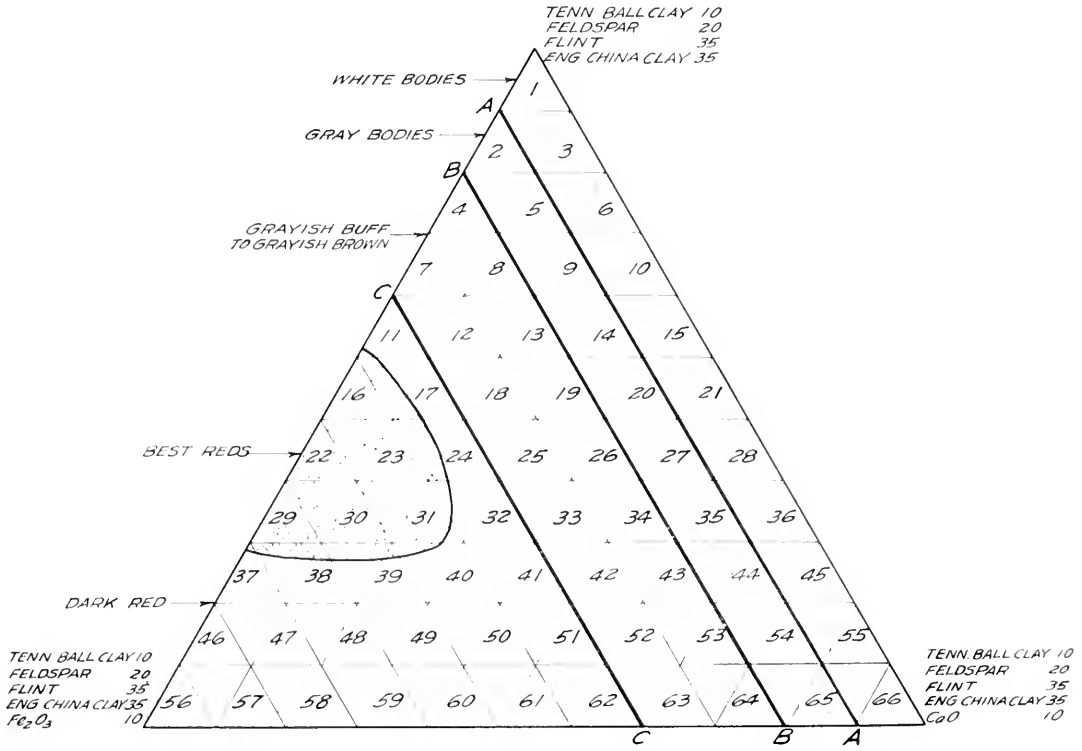
Good red bodies can be made by mixing the proper amounts of feldspar and flint with "Helmstadter" clay, and burning to practically complete vitrification.

This clay is very fine grained, plastic, and is red in color. The original red color of the clay is only slightly altered during burning, up to the point when the porosity is reduced to about three percent. A higher temperature causes the red color to deepen and gradually change to dark brown and finally black. The deepening of the color begins about cone 6, and by cone 8 the body is dark brown to black. The burning qualities of this clay seem to be due to the fact that the iron is present in a highly disseminated state.

This investigation was made to determine whether uniform colors of iron in varying shades could be produced by precipitating the chlorides of iron and calcium in a body.

A cone 10 porcelain was chosen for the body. It is not considered an ideal one for the production of red tile, and one containing more ball clay in place of the china clay would probably be better, since it would have less porosity in the dry state and would require less fluxing action for complete vitrification on that account.

Procedure. The three corner bodies as shown on the tri-axial diagram were mixed by wet-grinding for five hours in a porcelain-lined ball-mill. The tri-axial group of 66 bodies was made by blending these three bodies.


TENN BALL CLAY 10
FELDSPAR 20
FLINT 35
ENG CHINA CLAY 35
WHITE BODIES
GRAY BODIES
GRAYISH BUFF TO GRAYISH BROWN
BEST REDS
DARK RED
A
B
C
1
2
3
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66
TENN BALL CLAY 10
FELDSPAR 20
FLINT 35
ENG CHINA CLAY 35
Fe2O3 10
TENN BALL CLAY 10
FELDSPAR 20
FLINT 35
ENG CHINA CLAY 35
CoO 10

The mixtures were put in fruit jars and shaken thoroughly so as to obtain uniform mixtures. The chlorides were precipitated by adding NH_4OH and $(NH_4)_2CO_3$ and shaking. The slips were allowed to stand for a day, after which they were poured into plaster molds. When the excess water had been absorbed the bodies were removed from the molds, and dried in an oven to 200° C. After crushing in a porcelain mortar, triangular floor-tile were made by the dry-press process, about 10 percent of water being used. They were burned to cones 5, 7, 9 and 11 in an open, down-draft, gas-fired test kiln.

Results. Those bodies high in iron were most plastic, and those high in lime were least plastic. This was shown both by the working properties of the bodies in the plastic state and by the strength of the dried tile.

Vitrification—None of the bodies were completely vitrified at cone 5, although those high in iron and lime were hard and dense, those high in lime being the hardest. At cone 7, all bodies containing over four percent of fluxes were vitrified. All bodies were completely vitrified at cone 9, those containing over 7 percent of fluxes being overburned.

Bodies containing 4 percent and over of fluxes were overburned at cone 11. The remainder retained their shape but had a glassy surface with the exception of 1, 2 and 3.

Color—Bodies free from iron burned white and were practically uniform in color at vitrification.

Those containing 1 percent of iron were cream colored when burned under oxidizing conditions, but a good uniform gray color was obtained when the tile were reduced at the end of the burn. The lime had very little effect upon the color of bodies containing 1 percent of iron. Bodies containing 2 percent of iron were pink or light red at cone 5, above which temperature they changed to brownish buff with the exception of No. 4, which became dark yellowish gray.

Bodies containing 4 to 10 percent of iron burned red to dark red at cone 5. Those containing 4, 5 and 6 percent were still red at cone 7. The color was much deeper than at cone 5 and in-

creased with increased iron. Two percent of lime did not affect the color of bodies containing 5 percent or over of iron.

The remainder of the series did not produce desirable colors for floor tile.

CONCLUSIONS

Uniform gray colors of pleasing shades can be made by precipitating 0 to 2 percent of iron in a porcelain body and burning properly.

Uniform red colors can be produced by precipitating 4 to 6 percent of iron in a porcelain body which, if burned properly, would not have more than 3 to 4 percent porosity.

Ceramic Laboratory,
University of Illinois

DISCUSSION

Mr. Parmelee: I should like to ask the reason for using calcium salt.

Mr. Radcliffe: Calcium chloride was added, because it is a soluble salt; and it was thought, that the intimate mixture of the calcium and iron obtained in this way, might throw some light on the cause of the varied color effect, produced by iron in different clays.

SOME COBALT-URANIUM COLORS

BY B. S. RADCLIFFE

There are four coloring oxides, namely, copper, chromium, nickel and iron, which under proper conditions produce green colors in bodies and glazes. In physical mixtures, we are able to produce greens by blending blue and yellow.

The object of this investigation was to determine whether green could be produced by blending cobalt-blue and uranium-yellow.

Series A was made up as follows:

TABLE I—SERIES A

	A_1	A_2	A_3	A_4	A_5
Co_2O_3	1.0	0.9	0.8	0.7	0.6
$Na_2U_2O_7$ 6 H_2O	50.0	50.0	50.0	50.0	50.0
$Al_2(OH)_6$	40.0	40.0	40.0	40.0	40.0
ZnO	25.0	25.0	25.0	25.0	25.0

The stains were thoroughly mixed, calcined to cone 5, ground to pass a 200 mesh screen and added to a mat glaze having the formula,

$$\left.\begin{matrix} 0.1\ K_2O \\ 0.2\ CaO \\ 0.7\ PbO \end{matrix}\right\} 0.36\ Al_2O_3\ \ 1.36\ SiO_2$$

The glaze was then burned to cone 05. The result was a yellowish green glaze with blue specks. This was due to the fact that the cobalt was not thoroughly disseminated.

A blue stain

Co_2O_3	10
Calc. Al_2O_3	45
ZnO	45

was then made, calcined to cone 7, and ground to pass a 200 mesh screen.

Three frits were made using the mat glaze as before.

TABLE II—SERIES B

	B_1	B_2	B_3
Feldspar	17.6	17.6	17.6
$CaCO_3$	6.3	6.3	6.3
Red lead	50.5	50.5	50.5
Eng. china clay	11.0	11.0	11.0
Tenn. ball clay	10.0	10.0	10.0
Flint	4.6	4.6	4.6
Blue stain	10.0	10.0	10.0
$Na_2U_2O_7\ 6\ H_2O$	25.0	35.0	45.0

When applied as glazes, B 1 gave an olive green, B 2 and B 3 rich chocolate browns. These results indicate that the ratio of uranium to cobalt is too high.

The next step tried was to use the nitrates of cobalt and uranium, by fritting in the mat glaze.

TABLE III—SERIES C

	C_1	C_2	C_3
Feldspar	17.6	17.6	17.6
$CaCO_3$	6.3	6.3	6.3
Red lead	50.5	50.5	50.5
Eng. china clay	11.0	11.0	11.0
Tenn. ball clay	10.0	10.0	10.0
Flint	1.6	4.6	4.6
Cobalt nitrate	3.5	3.5	3.5
Uranium nitrate	10.0	12.0	15.0

The frits were ground, and a series of glazes made by blending with the original mat glaze.

Bright glazes were made by adding 20 parts of flint to the frits of this series.

The mat glazes were olive green, C_1 having a bluish shade.

Of the bright glazes C_3 was deep green in color, and C_1 and C_2 were green with a bluish shade.

Conclusions: Green glazes and mats can be made by blending cobalt and uranium in the right proportions, which is between four and five parts of uranium nitrate to one part of cobalt nitrate.

Ceramic Laboratory,
University of Illinois.

DISCUSSION

Prof. Orton: I do not know, whether there has ever been any report made, about the peculiar green developed by one of the roofing-tile plants in this country by the use of cobalt oxide and sulphate of antimony. These coarsely ground chemicals were added to a roughly prepared glaze; and the result was that they succeeded in getting a very passable green. At least it looked like a good green on the roof, but if looked at close by, the size of the blue and yellow spots was so large as to be offensive. The reason, that they did this, was that they were working in a sulphurous close atmosphere, that spoiled other greens, and they thought, that if they had a sulphate to start with, it would not do any harm.

Mr. Radcliffe: I might say that a man in the terra-cotta business in Kansas told me that he used cobalt and uranium to produce greens. He did not tell me, however, until we worked it out. He was using it for polychrome work. The cobalt-uranium green that he produced was better than any other green that he could make for this purpose. It did not run or blend off with the white, but instead he could get a firm line between the green and the white, or whatever base was beneath the green polychrome work.